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(21) International Application Number: PCT/US95/07911 (22) International Filing Date: 21 June 1995 (21.06.95) (30) Priority Data: 08/265,364 24 June 1994 (24.06.94) US (71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US). (72) Inventors: WELBORN, Howard, Curtis, Jr. (deceased). WALZER, John, Flexer, Jr.; 1901 Lakeside #902, Seabrook, TX 77586 (US). SAGAR, Vispi, Rustom; 2105 Olympic Drive, League City, TX 77573 (US). POIROT, Eugene, Edmond; 105 Caldwell Drive, Baytown, TX 77520 (US). CANICH, Jo Ann, Marie; Apartment 808, 900 Henderson Avenue, Houston, TX 77058 (US). BURKHARDT, Terry, John; 3111 Plaza Pines Drive, Kingwood, TX 77345 (US). (74) Agents: SHER, Jaimes et al.; Exxon Chemical Company, P.O. Box 2149, Baytown, TX 77522 (US).		(81) Designated States: CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>With amended claims and statement.</i>
(54) Title: POLYMERIZATION PROCESS AND CATALYST SYSTEMS USEFUL THEREIN (57) Abstract This invention relates to polymerization processes and to catalyst systems useful therein. Particularly, the invention relates to metallocene catalysts useful in a continuous gas phase polymerization process for producing high molecular weight polymers.		

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**POLYMERIZATION PROCESS AND CATALYST SYSTEMS USEFUL
THEREIN**

FIELD OF THE INVENTION

5 This invention relates to polymerization processes and to catalyst systems useful therein. Particularly, the invention relates to metallocene catalysts useful in a continuous gas phase polymerization process for producing high molecular weight polymers.

BACKGROUND OF THE INVENTION

10 A new catalyst technology has developed which provides for the modification and/or control over the properties and characteristics of a polymer. This technology principally involves the general field of transition metal catalysis.

 These new catalysts are referred to as bulky ligand transition metal catalysts which are formed from a bulky ligand transition metal compound and an activator.

15 The bulky ligand of the transition metal compound may contain a multiplicity of bonded atoms, preferably carbon atoms and typically contain a cyclic structure such as, for example, a cyclopentadienyl ligand or a substituted cyclopentadienyl ligand, or any other ligand capable of η -5 bonding to the transition metal atom. The transition metal is typically a Group 4, 5 or 6 transition metal or may be a

20 metal from the lanthanide and actinide series. Other ligands may be bonded to the transition metal, such as but not limited to hydrocarbyl, halogen or any other univalent anionic ligand. Generally in the art, these bulky ligand catalysts are referred to as metallocene catalysts.

 Metallocene catalysts are useful in solution-phase, slurry phase, gas phase

25 and high pressure polymerization processes. When using metallocenes with a low degree of substitution on the cyclopentadienyl ring (e.g., bis-methylcyclopentadienyl zirconium dichloride) in a gas phase polymerization process, high molecular weight polymers can be difficult to produce, especially polymers having fractional melt indices.

30 One means of solving this problem in the art would be to use a cost prohibitive hydrogen removal system in the feed or recycle system. Such hydrogen removal systems, commonly referred to as "hydrogen scrubbers," have been used with traditional Ziegler-Natta catalyst systems. These scrubbers typically contain a hydrogenation catalyst. Hydrogenation catalysts generally contain a noble metal

35 such as palladium, platinum, rhodium and ruthenium on a support material, for example alumina. For more details on hydrogenation catalysts and hydrogen

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removal systems, see U.S. Patent Nos. 3,146,223, 4,200,714 and 4,851,488. U.S. Patent 4,851,488 also describes a nickel catalyst useful for removing hydrogen.

Use of a hydrogenation catalyst in a process where the catalyst feed stream contains terminal olefins is problematic, because a significant amount of isomerized products (e.g., 2-hexene from 1-hexene) can be formed. Typically these internal olefins are difficult to polymerize and can eventually build up to such a level so as to detrimentally affect polymerization.

Thus, a need exists in the industry for a metallocene catalyst, especially useful in a continuous gas phase polymerization process, for the production of high molecular weight polymers, without the need for an expensive and complicated hydrogen removal system.

SUMMARY OF THE INVENTION

This invention generally relates to catalysts particularly useful in a continuous gas phase polymerization process for producing high molecular weight polymers. The invention specifically relates to a gas phase polymerization process utilizing particular metallocene catalysts to produce polymers having low melt indices.

The metallocene catalyst of the invention is generally a substituted bis-(cyclopentadienyl) Group 4, 5 or 6 transition metal catalyst, where independently each cyclopentadienyl ligand is substituted with one or more hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals, disubstituted boron radicals, disubstituted pnictogen radicals, substituted chalcogen radicals or halogen radicals or two adjacent radical groups are joined forming a ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand and such that the total number of substituent groups, on all cyclopentadienyl ligands, are in the range of 3 to 8.

In a preferred embodiment, the polymerization process of the invention utilizes the catalyst described above in a continuous gas phase polymerization process. The polymers produced by the process of the invention in one embodiment, have melt indices in the range of from 0.01 to less than about 5 dg/min.

DETAILED DESCRIPTION OF THE INVENTION

Introduction

The invention relates to a gas phase polymerization process for producing polymers having a high molecular weight in the presence of metallocene catalysts,

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specifically bulky ligand transition metal catalysts. While there are many metallocene catalysts described in the art, these catalyst generate an excess of hydrogen, particularly in a gas phase polymerization process. The hydrogen generated in a gas phase process limits the production of high molecular weight polymers. In a continuous gas phase process where a recycle stream is employed, hydrogen concentration builds in the system to a steady state value incompatible with the production of high molecular weight polymer. Thus, without a removal system such as a hydrogen scrubber, high molecular weight polymers, particularly those with fractional melt indices are difficult to produce.

Applicants have discovered a specific group of metallocene catalysts that are capable of producing very low melt index products in a gas phase polymerization process. The metallocene catalysts of the invention are significantly less sensitive to hydrogen, or in other words, produce less hydrogen, or in the presence of hydrogen still produce high molecular weight polymers.

It has been discovered that those metallocenes with a low degree of substitution on the cyclopentadienyl ring generate a significant amount of hydrogen during polymerization. The amount of hydrogen generated by these metallocenes limits their ability to produce low melt index polymers.

It has also been discovered that the concentration of hydrogen build-up in a reactor using these metallocenes increases to a steady state such that these metallocene's ability to produce fractional melt index polymer is very difficult, if not impossible.

Catalyst and Catalyst Systems

The transition metal component of the metallocene catalyst of this invention is a Group 4, 5 or 6 transition metal compound containing ligands capable of η -5 bonding to the metal center (formally donating six electrons to the metal). Such ligands include substituted and unsubstituted cyclopentadienyl ligands, and η -5 bonding aromatic heterocycles including but not limited to heterocycles containing Group 15 and 16 elements, especially nitrogen, oxygen, phosphorus and sulfur, and non-carbon Group 14 elements, especially silicon and germanium wherein the ligands capable of η -5 bonding to the metal center are substituted with at least three substituent groups in total. Other ligands may be bonded to the transition metal, such as but not limited to hydrocarbyl, halogen or any other univalent anionic ligand.

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The preferred Group 4 transition metals are zirconium, hafnium and titanium, the most preferred being zirconium. The transition metal may be in any oxidation state, preferably +3 or +4 or a mixture thereof, and +4 is most preferred.

The metallocene catalyst component of the invention is activated as has been well established in the art by alumoxane and/or ionizing activators or any other activator. For examples of activators useful in this invention, see EP-A-0 520 732, EP-A-0 277 003, EP-A-0 277 004, EP-A-0 520 732 and EP-A-0 500 944 and U.S. Patent Nos. 5,153,151, 5,198,401, 5,241,025, 5,241,025, 5,057,475, 5,017,714 and 5,324,800, all of which are herein incorporated by reference for U.S. patent practice purposes.

More commonly, the transition metal component of the metallocene catalyst of this invention are generally substituted bis(cyclopentadienyl) Group 4 transition metal catalysts where the cyclopentadienyl rings are substituted with hydrogen, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radical, substituted halocarbyl radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted organometalloid radicals, disubstituted boron radicals, disubstituted pnictogen radicals, substituted chalcogen radicals, or halogen radicals.

In general, these compounds may be represented by the following general formula:



wherein:

M is a Group 4 metal especially zirconium, hafnium and titanium;

$(C_5H_{5-x}R_x)$ and $(C_5H_{5-y}R_y)$ are independently a cyclopentadienyl ring substituted with from zero to five R radicals;

x is from 0 to 5 denoting the degree of substitution, y is from 0 to 5 denoting the degree of substitution, and x + y equals 3, 4, 5, 6, 7, or 8.

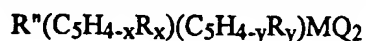
each R substituent is, independently, a radical group which is a C₁₋₃₀ hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid radical, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen or two adjacent R groups are joined forming a C₄ to C₃₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

Q are independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, or two Q are

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joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms or may be an alkylidene; or if the activator component is an alumoxane or other Lewis acid activators capable of alkylating the metal component, Q may be any anionic univalent ligand provided that Q is not a cyclopentadienyl ligand and would additionally include halogens, alkoxides, aryloxides, amides and phosphides.

In another embodiment, the metallocene catalyst component is a bridged metallocene catalyst component represented by the following formula:



wherein:

M is a Group 4 metal especially zirconium, hafnium and titanium;

$(C_5H_4-xR_x)$ and $(C_5H_4-yR_y)$ are independently a cyclopentadienyl ring substituted with from zero to four R radicals;

x is from 0 to 4 denoting the degree of substitution, y is from 0 to 4 denoting the degree of substitution, and x + y equals 3, 4, 5, 6, 7, or 8.

each R substituent is, independently, a radical group which is a C₁₋₃₀ hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid radical, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen or two adjacent R groups are joined forming a C₄ to C₃₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

Q are independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, or two Q are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms or may be an alkylidene; or if the activator component is an alumoxane or any other Lewis acid activator capable of alkylating the transition metal component, Q may be any anionic univalent ligand provided that Q is not a cyclopentadienyl ligand and would additionally include halogens, alkoxides, aryloxides, amides and phosphides;

and R'' is one or more of, or a combination of, a carbon, a germanium, a silicon, a phosphorous or a nitrogen atom containing radical bridging the $(C_5H_4-xR_x)$ and $(C_5H_4-yR_y)$ rings including but not limited to R'₂C, R'₂Si, R'₂SiR'₂Si, R'₂SiR'₂C, R'₂Ge, R'₂SiR'₂Ge, R'₂GeR'₂C, R'N, R'P, R'₂CR'N, R'₂CR'P, R'₂SiR'N, R'₂SiR'P, R'₂GeR'N, R'₂GeR'P where each R' is independently, a radical group which is hydride, C₁₋₃₀ hydrocarbyl, substituted hydrocarbyl, halocarbyl,

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substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen.

Illustrative, but non-limiting examples of R radicals are C₁₋₂₀ hydrocarbyl radicals including methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, phenyl, tolyl, benzyl, ethenyl, propenyl and isomers thereof; halocarbyl radicals including fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl, chlorobenzyl and isomers thereof; hydrocarbyl-substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyl-diethylsilyl and the like; halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)silyl, methylbis(difluoromethyl)silyl, tris(trifluoromethyl)germyl, bromomethyldimethylgermyl and the like; disubstituted boron radicals including dimethylboron, diethylboron, diphenylboron, dipropylboron, bis-tolylboron, methylpropylboron and isomers thereof; disubstituted pnictogen radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, dipropylamine, dibutylamine and isomers thereof; substituted chalcogen radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide, ethylsulfide, butylsulfide, tolylsulfide and isomers thereof, or halogen radicals including fluoro, chloro, bromo or iodo; or two adjacent R groups are joined forming a C₄ to C₂₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand

Illustrative, but non-limiting examples of Q radicals include hydride, methyl, ethyl, phenyl, propyl, butyl, amyl, hexyl, cyclohexyl, heptyl, tolyl, trifluoromethyl, tetramethylene and pentamethylene (both Q), methylidene (both Q) trimethylsilyl, triphenylsilyl, and tris(trimethylsilyl)methyl including isomers thereof if any exist. Additionally if the activator component is an alumoxane Q can additionally be chloro, bromo, iodo, fluoro, methoxy, ethoxy, propoxy, phenoxy, dimethylamide, dimethylphosphide and the like.

Illustrative but non-limiting examples of R" bridging groups include dimethylsilyl, diethylsilyl, methylethylsilyl, trifluoromethylbutylsilyl, bis(trifluoromethyl)silyl, di-n-butylsilyl, di-i-propylsilyl, dicyclohexylsilyl, diphenylsilyl, cyclohexylphenylsilyl, t-butylcyclohexylsilyl, di-t-butylsilyl, t-butylphenylsilyl, di(p-tolyl)silyl, dimethylgermyl, diethylgermyl, ethylmethylgermyl, methylphenylgermyl, diphenylgermyl, methylene, dimethylmethylene, diphenylmethylene, ethylene, 1,2-dimethylethylene, 1,2-diphenylethylene, 1,1,2,2-tetramethylethylene, dimethylmethylenedimethylsilyl, methylenediphenylgermyl,

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methylamine, phenylamine, cyclohexylamine, methylphosphine, phenylphosphine, cyclohexylphosphine and the like.

Illustrative but non-limiting examples of cyclopentadienyl and substituted cyclopentadienyl ligands include cyclopentadienyl, methylcyclopentadienyl, 1,2-
 5 dimethylcyclopentadienyl, 1,3-dimethylcyclopentadienyl, 1,3,5-trimethylcyclopentadienyl, tetramethylcyclopentadienyl, 1-methyl-3-butylcyclopentadienyl, n-butylcyclopentadienyl, 1,2-di-n-butylcyclopentadienyl, t-butylcyclopentadienyl, cyclohexylcyclopentadienyl, 1-methyl-3-cyclohexylcyclopentadienyl, phenylcyclopentadienyl,
 10 trifluoromethylcyclopentadienyl, indenyl, tetrahydroindenyl, trimethylsilylcyclopentadienyl, trimethylgermylcyclopentadienyl, dimethylaminocyclopentadienyl, diphenylphosphinocyclopentadienyl, and fluorocyclopentadienyl and pentamethylcyclopentadienyl (non-bridged compounds only).

15 In one embodiment of the invention, the cyclopentadienyl rings are substituted such that the number, kind and placement of substituents on each ring is the same, for example, but not limited to, bis(1,3-dimethylcyclopentadienyl)zirconium dichloride, bis(tetramethylcyclopentadienyl)zirconium dichloride, bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dichloride, bis(1-ethyl-3-n-butylcyclopentadienyl)hafnium dimethyl, methylene bis(1,3-dimethylcyclopentadienyl)titanium dichloride, dimethylsilyl bis(1,2-dimethylcyclopentadienyl)hafnium dibenzyl and the like.

25 In another embodiment of the invention, the cyclopentadienyl rings are substituted such that the number, kind or placement of substituents on each ring is different, for example, but not limited to, (cyclopentadienyl)(tetramethylcyclopentadienyl)zirconium dichloride, (cyclopentadienyl)(pentamethylcyclopentadienyl)zirconium dichloride, (methylcyclopentadienyl)(pentamethylcyclopentadienyl)zirconium dichloride, (1-methyl-3-n-butylcyclopentadienyl)(tetramethylcyclopentadienyl)hafnium dichloride,
 30 (cyclopentadienyl)(1,2,4-trimethylcyclopentadienyl)titanium dimethyl, dimethylsilyl(cyclopentadienyl)(tetramethylcyclopentadienyl)hafnium dimethyl, ethylene(methylcyclopentadienyl)(tetramethylcyclopentadienyl)titanium dichloride and the like.

35 In the preferred embodiment of the invention, $x + y$ equals 5, 6, 7 or 8.

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For purposes of this patent specification the term "carrier" or "support" are interchangeable and can be any support material, preferably a porous support material, such as for example, talc, inorganic oxides, inorganic chlorides and resinous support materials such as polyolefin or polymeric compounds or any other organic support material.

The preferred support materials are inorganic oxide materials, which include those from the Periodic Table of Elements of Groups 2, 3, 4, 5, 13 or 14 metal oxides. In a preferred embodiment, the catalyst support material includes silica, alumina, silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania, zirconia, and the like.

Polymerization Process

The catalyst system of this invention is particularly well suited for the polymerization of monomers, optionally with comonomers in any gas phase polymerization or prepolymerization process or combination thereof.

In the preferred embodiment, this invention is directed toward a gas phase polymerization reaction involving the polymerization of one or more olefins, monoolefins, diolefins, cyclic olefins, acetylenically unsaturated monomers, ethylenically unsaturated non-cyclic non-conjugated polyenes, cyclic non-conjugated polyenes and combinations thereof. Preferably, the monomers are ethylene and alpha-olefins having from 3 to 20 carbon atoms, most preferably 3 to 12 carbon atoms. The invention is particularly suitable for polymerization reactions involving polymerization of one or more of the monomers, for example alpha-olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methylpentene-1, hexene-1, octene-1, decene-1, cyclic olefins such as norbornene and alpha-olefins substituted with aryl groups such as styrene. Other monomers can include diolefins such as 1,5-hexadiene, 1,7-octadiene, norbornadiene, vinylnorbornene, and the like, and acetylene and substituted allcynes.

In another embodiment, ethylene is polymerized with at least two comonomers to form a terpolymer and the like. Most preferred comonomers for polymerization with ethylene are butene-1, pentene-1, hexene-1, 4-methyl-1-pentene and octene-1.

In another embodiment of the process of the invention, the olefin(s) are prepolymerized in the presence of the catalyst system of the invention prior to the main polymerization. The prepolymerization can be carried out batchwise or continuously in gas, solution or slurry phase including at elevated pressures. For

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details on prepolymerization see, for example U.S. Patent No. 4,923,833 and 4,921,825 and EP-B-0279 863, published October 14, 1992 all of which are incorporated fully herein by reference.

5 In a gas phase polymerization process a continuous cycle is typically employed wherein one part of the cycle of a reactor, a cycling gas stream (otherwise known as a cycle gas stream or fluidizing medium) is heated in the reactor by the heat of polymerization. This heat is removed in another part of the cycle by a cooling system external to the reactor.

10 Generally, in a gas fluidized bed process for producing polymer from monomers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. (See for example U.S. Patent Nos. 4,543,399, 4,588,790, 5,352,749 and 5,405,922, all fully incorporated herein by reference for U.S. patent 15 practice purposes.) It is within this cycle gas stream that hydrogen generated by the catalyst within the reactor is cycled back into the reactor. Without a hydrogen removal system this accumulation of hydrogen within the system complicates the production of low melt index polymers.

20 In one embodiment of the invention a process is provided wherein the cycle gas stream contains less than 500 preferably less than 400, more preferably less than 300 and most preferably less than 200 ppm hydrogen.

25 In another embodiment, the ratio of $(C_x + H_2)/C_y$ in the cycle gas composition entering the reactor is less than 0.2, where C_x is the mole percent of comonomer, for example, hexene-1 and/or butene-1 and C_y is the mole percent of monomer, for example, ethylene and/or propylene.

Polymer Produced by the Process of the Invention

30 The polymer product of the invention has a density in the range of from 0.87 g/cc to about 0.97 g/cc, preferably 0.88 g/cc to about 0.96 g/cc, more preferably 0.90 g/cc to about 0.95 g/cc and even more preferably 0.91 g/cc to about 0.94 g/cc and most preferably 0.912 g/cc to about 0.935 g/cc.

35 MWD, or polydispersity, is a well known characteristic of polymers. MWD is generally described as the ratio of the weight average molecular weight (M_w) to the number average molecular weight (M_n). The ratio M_w/M_n can be measured directly by gel permeation chromatography techniques, or indirectly, by measuring the ratio of I_{21} to I_2 as described in ASTM D-1238-F and ASTM D-1238-E respectively. I_2 is well known in the art as equivalent to Melt Index (MI).

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I_{21} is also known as high load melt index (HLMI). MI is inversely proportional to the molecular weight of the polymer (M_w).

The melt index of the polymers of the invention range are generally in the between from about 5 dg/min to about 0.01 dg/min, preferably about 3 dg/min to about 0.10 dg/min and most preferably less than about 1 dg/min to about 0.10 dg/min.

The MWD of the polymers of the invention are in the range of greater than about 1.5 to about greater than 20, preferably in the range of greater than about 2.0 to about 10 and most preferably in the range of about 2.5 to about 7.

The ratio of I_{21}/I_2 is known as the melt index ratio (MIR) and for the purposes of this patent specification the ratio is also defined to be melt flow ratio (MFR). MIR is generally proportional to the MWD.

The MIR of the polymers of this invention are generally in the range of greater than 10 to about 200, preferably about 12 to about 60 and most preferably about 14 to about 45.

The M_w of the polymers of the invention are typically greater than 100,000 more preferably greater than 105,000 and even more preferably greater than 110,000 and most preferably greater than 120,000. The high load melt index (HLMI) for the polymers of the invention is in the range of about 1 to 50.

The polymers produced by the process of the invention are useful in such forming operations as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films in mono-layer or multilayer constructions formed by coextrusion or by lamination. Such films are useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fiber forming operations include melt spinning, solution spinning and melt blown fiber operations. Such fibers may be used in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. General extruded articles include medical tubing, wire and cable coatings, geomembranes, and pond liners. Molded articles include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

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EXAMPLES

In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered.

For the purposes of this patent specification the M_w (molecular weight) of a polymer is determined with a Waters Gel Permeation Chromatograph equipped with ultra styrogel columns and a refractive index detector. The operating temperatures of the instrument was set at 145°C, the eluting solvent was trichlorobenzene, and the colchration standards include sixteen polystyrenes of precisely known molecular weight, ranging from a M_w of 500 to a M_w of 5.2 million, and a polyethylene standard, NBS 1475.

EXAMPLE 1

Catalyst Preparation

Each of 0.6 grams of cyclopentadienyl(tetramethylcyclopentadienyl) zirconium dichloride (Catalyst A), 0.6 grams of cyclopentadienyl (pentamethylcyclopentadienyl) zirconium dichloride (Catalyst B), 0.6 grams of methylcyclopentadienyl(pentamethylcyclopentadienyl) zirconium dichloride (Catalyst C), 0.6 grams of bis(tetramethylcyclopentadienyl) zirconium dichloride (Catalyst D), and 0.6 grams of bis(1-n-butyl-3-methyl cyclopentadienyl) zirconium dichloride (Catalyst E) were separately dissolved in 180 cc of dry toluene at 25 °C under nitrogen in a 500 cc round bottom flask while stirring with a magnetic stirrer. Stirring was continued for 15 minutes, at which time 39.6 cc of 10 wt% methylalumoxane was slowly added. After stirring the resulting solution for an additional 15 minutes, 24.0 grams of a high surface area (Davison 948) silica dehydrated at 800°C was added over a period of 10 minutes. This suspension was then stirred for twenty minutes. The toluene was then removed in vacuo at 50 °C, and the remaining catalyst dried at this temperature for 4 hours.

POLYMERIZATION TESTS

A sample of each of the metallocenes A-E supported on the treated silica as described above was used for ethylene/1-hexene copolymerization studies as described below. A continuous fluid bed gas-phase reactor operated at 300 psig (2069 kPa) total pressure, 145°F (63°C) reactor temperature and 0.7 ft/s (21.3 cm/s) cycle gas velocity was used for determining catalyst efficiency and response to co-monomer such as 1-hexene. A solution of TEAL (1 wt% in isopentane) was fed into the reactor as a scavenger at a rate of 1 cm³/h. A detailed composition of ethylene and 1-hexene composition produced is included in Table 1, along with the

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process data. Polymer samples were collected and analyzed after three bed turnovers.

While the present invention has been described and illustrated by reference to particular embodiments, it will be appreciated by those of ordinary skill in the art that the invention lends itself to variations not necessarily illustrated herein. For
5 example, it is not beyond the scope of this invention to further use a hydrogen scrubber to even further lower molecular weight or to use at least one of the metallocene catalysts of the invention with any other metallocene catalyst in one or more reactors, separately or together. For this reason, then, reference should be
10 made solely to the appended claims for the purposes of determining the true scope of the present invention.

TABLE I

Catalyst	A	B	C	D	E
Metallocene	Cp(Me ₄ Cp)ZrCl ₂	CpCp*ZrCl ₂	MeCpCp*ZrCl ₂	(Me ₄ Cp) ₂ ZrCl ₂	(MeBuCp) ₂ ZrCl ₂
PROCESS DATA					
H ₂ conc. (ppm)	143	123	123	125	127
C ₆ /C ₄ conc. (mol%)	0.94	0.87	0.99	0.94	0.86
C ₂ conc. (mol%)	31.9	28.9	30.7	32.3	31.1
H ₂ /C ₂ mole ratio x 1000	4.5	4.3	4.0	3.9	4.1
C ₆ mole ratio	0.029	0.030	0.032	0.029	0.028
Reactor Temp °F (°C)	144 (62.2)	143 (61.6)	143 (61.6)	143 (61.6)	144 (62.2)
POLYMER DATA					
MI	1.02	0.50	0.18	0.28	1.31
HLMI	46.00	13.54	7.05	9.56	26.29
Density g/cc	0.913	0.916	0.916	0.916	0.917
M _w	92,000	115,000	124,000	113,000	93,000
MWD	6.4	3.8	3.9	4.0	2.7
Productivity (g of polymer/g of catalyst)	200	700	700	500	700
x + y =	4	5	6	8	4

Cp* indicated a cyclopentadienyl ring containing all methyl substituents.

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CLAIMS

We Claim:

1. A continuous process for polymerizing olefins alone or in combination with
5 one or more other olefins in a gas phase polymerization process for producing
polymers, said process for polymerizing olefins comprising the steps of:
 - a) introducing monomer and optionally a comonomer in the presence
of a catalyst system comprising:
 - i) a substituted bis(cyclopentadienyl) Group 4, 5 and 6
10 transition metal metallocene component where independently each
cyclopentadienyl ligand is substituted with one or more hydrocarbyl radicals,
substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl
radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted
organometalloid radicals, disubstituted boron radicals, disubstituted pnictogen
15 radicals, substituted chalcogen radicals or halogen radicals or two adjacent radical
groups are joined forming a ring to give a saturated or unsaturated polycyclic
cyclopentadienyl ligand and such that the total number of substituent groups, on all
cyclopentadienyl ligands, are in the range of 3 to 8; and
 - ii) an activator for said metallocene component; and
 - b) withdrawing a polymer product having a melt index in the range of
20 from 0.01 to 5 dg/min.
2. A continuous process for polymerizing olefins alone or in combination with
one or more other alpha-olefins in a gas phase polymerization reactor having a
25 fluidizing medium and a fluidized bed, said process comprising passing a gaseous
stream comprising monomer(s) through a reaction zone in the presence of a
catalyst system to produce a polymeric product, withdrawing said fluidizing
medium comprising unreacted monomer from said reaction zone, mixing said
fluidizing medium with polymerizable monomer(s), and recycling said fluidizing
30 medium to said reactor, the catalyst system comprising:
 - i) a substituted bis (cyclopentadienyl) Group 4, 5 and 6
transition metal metallocene component where independently each
cyclopentadienyl ligand is substituted with one or more hydrocarbyl radicals,
substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl
35 radicals, hydrocarbyl-substituted organometalloid radicals, halocarbyl-substituted
organometalloid radicals, disubstituted boron radicals, disubstituted pnictogen

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radicals, substituted chalcogen radicals or halogen radicals or two adjacent radical groups are joined forming a ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand and such that the total number of substituent groups, on all cyclopentadienyl ligands, are in the range of 3 to 8; and

- 5 ii) an activator for said metallocene component; and said polymer product having a melt index in the range of 0.10 to .05 dg/min.

3. The process in accordance with any preceding claim wherein the metallocene component is represented by the following formula:



wherein:

M is a Group 4 metal, preferably hafnium or zirconium;

$(C_5H_{5-x}R_x)$ and $(C_5H_{5-y}R_y)$ are independently a cyclopentadienyl ring substituted with from zero to five R radicals;

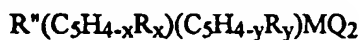
- 15 x is from 0 to 5 denoting the degree of substitution, y is from 0 to 5 denoting the degree of substitution, and $x + y$ equals 3, 4, 5, 6, 7, or 8.

each R substituent is, independently, a radical group which is a C₁₋₃₀ hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid radical, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or
20 halogen or two adjacent R groups are joined forming a C₄ to C₃₀ ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand;

Q are independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and
25 hydrocarbyl- and halocarbyl-substituted organometalloid radicals, an anionic univalent ligand, halogen, alkoxide radicals, aryloxide radicals, amide radicals, phosphide radicals or a combination thereof, or two Q are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms or an alkylidene.

30

4. The process in accordance with any preceding claim wherein the metallocene catalyst component is a bridged metallocene catalyst component represented by the following formula:



35 wherein:

M is a Group 4 metal;

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($C_5H_{4-x}R_x$) and ($C_5H_{4-y}R_y$) are independently a cyclopentadienyl ring substituted with from zero to four R radicals;

x is from 0 to 4 denoting the degree of substitution, y is from 0 to 4 denoting the degree of substitution, and $x + y$ equals 3, 4, 5, 6, 7, or 8.

5 each R substituent is, independently, a radical group which is a C_{1-30} hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid radical, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen or two adjacent R groups are joined forming a C_4 to C_{30} ring to give a
10 saturated or unsaturated polycyclic cyclopentadienyl ligand;

Q are independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl- and halocarbyl-substituted organometalloid radicals, an anionic univalent ligand, halogen, alkoxide radicals, aryloxide radicals, amide radicals,
15 phosphide radicals, or a combination thereof, or two Q are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms or may be an alkylidene;

and R'' is one or more of, or a combination of, a carbon, a germanium, a silicon, a phosphorous or a nitrogen atom containing radical bridging the ($C_5H_{4-x}R_x$) and ($C_5H_{4-y}R_y$) rings including but not limited to R'_2C , R'_2Si , $R'_2SiR'_2Si$,
20 $R'_2SiR'_2C$, R'_2Ge , $R'_2SiR'_2Ge$, $R'_2GeR'_2C$, $R'N$, $R'P$, $R'_2CR'N$, $R'_2CR'P$, $R'_2SiR'N$, $R'_2SiR'P$, $R'_2GeR'N$, $R'_2GeR'P$ where each R' is independently, a radical group which is hydride, C_{1-30} hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-
25 substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen.

5. The process in accordance with any preceding claim wherein the total number of substituents bonded to the cyclopentadienyl ligand(s) is in the range of 4
30 to 8, preferable 5 to 8.

6. The process in accordance with any preceding claim wherein the polymer product has a melt index in the range of 0.05 to 3 dg/min, preferably from 0.01 dg/min to 3 dg/min, more preferably 0.5 dg/min to 2 dgmin.

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7. The process of claims 3 and 4 wherein x does not equal y or $x + y$ is 5, 6, 7 or 8 or x is 5 or x is 5 and y is 0.
8. The process of claim 2 wherein said fluidizing medium withdrawn from the
5 reaction zone comprises less than 200 ppm hydrogen.
9. The process of claim 2 wherein the polymer product has a molecular weight greater than 100,000, preferably greater than 110,000.
10. The process in accordance with any preceding claim wherein one
10 cyclopentadienyl ligand is substituted with hydrocarbyl groups having 1 to 20 carbon atoms, or the cyclopentadienyl ligand is substituted with at least four hydrocarbyl radicals having from 1 to 20 carbon atoms.

15

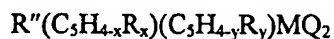
AMENDED CLAIMS

[received by the International Bureau on 22 November 1995 (22.11.95);
original claims 3, 7, 10 cancelled; original claims 1, 2, 4, 5, amended;
remaining claims unchanged (3 pages)]

- 5 1. A continuous process for polymerizing olefins alone or in combination with one or more other olefins in a gas phase polymerization process for producing polymers, said process for polymerizing olefins comprising the steps of:
- a) introducing monomer and optionally a comonomer in the presence of a catalyst system comprising:
- 10 i) a substituted *bis*(cyclopentadienyl) Group 4, 5, and 6 transition metal metallocene component represented by the formula:
- $$(C_5H_{5-x}R_x)(C_5H_{5-y}R_y)MQ_2$$
- wherein:
- 15 M is a Group 4 metal, preferably hafnium or zirconium;
($C_5H_{5-x}R_x$) and ($C_5H_{5-y}R_y$) are each independently a cyclopentadienyl ring substituted with from zero to five R radicals;
x is from 0 to 5 denoting the degree of substitution, y is from 0 to 5 denoting the degree of substitution, and x + y equals 4, 5, 6, 7, or 8,
20 and when x + y = 4, the number of substituents on each ring is different;
each R substituent is independently, a hydrocarbyl radical selected from the group consisting of methyl, ethyl, propyl, or butyl;
Q are independently, hydride radicals, hydrocarbyl radicals, substituted
25 hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl-and halocarbyl-substituted organometalloid radicals, an anionic univalent ligand, halogen, alkoxide radicals, aryloxy radicals, amide radicals, phosphide radicals or a combination thereof, or two Q are joined and bound to the metal
30 atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms or an alkylidene.
- ii) an activator for said metallocene component;
iii) a carrier; and
- b) withdrawing a polymer product having a melt index in the range of
35 from 0.01 to 5 dg/min.

2. The process of Claim 1 in a gas phase polymerization reactor having a fluidizing medium and a fluidized bed, said process comprising passing a gaseous stream comprising monomer(s) through a reaction zone in the presence of a catalyst system to produce a polymeric product, withdrawing said fluidizing medium comprising unreacted monomer from said reaction zone, mixing said fluidizing medium with polymerizable monomer(s), and recycling said fluidizing medium to said reactor.

4. The process in accordance with any preceding claim wherein the metallocene catalyst component is a bridged metallocene catalyst component represented by the formula:



wherein:

M is a Group 4 metal;

($C_5H_{4-x}R_x$) and ($C_5H_{4-y}R_y$) are each independently a cyclopentadienyl ring substituted with from zero to four R radicals;

x is from 0 to 5 denoting the degree of substitution, y is from 0 to 5 denoting the degree of substitution, and x + y equals 4, 5, 6, 7, or 8, and when x + y = 4, the number of substituents on each ring is different;

each R substituent is independently, a hydrocarbyl radical selected from the group consisting of methyl, ethyl, propyl, or butyl;

Q are independently, hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, and hydrocarbyl-and halocarbyl-substituted organometalloid radicals, an anionic univalent ligand, halogen, alkoxide radicals, aryloxide radicals, amide radicals, phosphide radicals, or a combination thereof, or two Q are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms or may be an alkylidene;

and R'' is one or more of, or a combination of, a carbon, a germanium, a silicon, a phosphorous or a nitrogen atom containing radical bridging the ($C_5H_{4-x}R_x$) and ($C_5H_{4-y}R_y$) rings including but not limited to R'_2C , R'_2Si , $R'_2SiR'_2Si$, $R'_2SiR'_2C$, R'_2Ge , $R'_2SiR'_2Ge$, $R'_2GeR'_2C$, R'_2N , R'_2P , $R'_2CR'_2N$, $R'_2CR'_2P$, $R'_2SiR'_2N$, $R'_2SiR'_2P$, $R'_2GeR'_2N$, $R'_2GeR'_2P$ where each R' is independently, a radical group which is hydride, C_{1-30} hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted

halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted pnictogen, substituted chalcogen, or halogen.

- 5 5. The process in accordance with any preceding claim wherein the total number of substituents bonded to the cyclopentadienyl ligand(s) is in the range of 5 to 8.
6. The process in accordance with any preceding claim wherein the polymer product has a melt index in the range of 0.05 to 3 dg/min., preferably from 0.01 dg/min. to 3 dg/min., more preferably 0.5 dg/min. to 2 dg/min.
- 10 8. The process of Claim 2 wherein said fluidizing medium withdrawn from the reaction zone comprises less than 200 ppm hydrogen.
- 15 9. The process of Claim 2 wherein the polymer product has a molecular weight greater than 100,000, preferably greater than 110,000.

STATEMENT UNDER ARTICLE 19

The invention of this application is addressed in major part to the problem of preparation of high molecular weight polyethylene copolymers utilizing metallocene catalysts in gas phase polymerization processes. The claims as amended require the presence of a catalyst carrier and a specific selection of substituted cyclopentadienyl ligands on the transition metal metallocene compounds. Support for the amendments appear in the text of the international application as filed at page 8, lines 1-10; page 6 lines 4-5; page 7, lines 24-34; and in both of Example 1 and Table 1. The International Search report accompanying this international application identifies both of EP-A- 0 593 083 and EP-A- 0 582 480 as being of particular relevance. However, the identified documents do not address the preparation of high molecular weight copolymers.

EP-A- 0 593 083 teaches the use of unsupported soluble transition coordination catalysts in gas phase polymerization. All examples of this document illustrate fused ring substituted cyclopentadienyl ligands, indenyl or fluorenyl. Such catalyst systems are not within the description scope of the amended claims.

EP-A- 0 582 480 illustrates in Examples 1 and 3 the use of bis(1-methyl-3-n-butylcyclopentadienyl) zirconium dichloride with a carrier. Though this catalyst is an effective catalyst for polyethylene copolymerization, the examples of Applicant's illustrate that under similar conditions, the catalysts of the amended claims are capable of producing lower melt index copolymers, thus of higher molecular weight, than those produced with that of Examples 1 and 3 in this document (Table 1). Examples A-D illustrate the use of claimed catalysts to prepare copolymers having melt indices of 0.18-1.02, whereas example E, the metallocene compound of this referenced document, illustrates a melt index of 1.31 (all in dg/min. units). This catalyst is outside the description coverage of the amended claims since $x+y = 4$ and the substituents on each cyclopentadienyl ring is the same.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/07911

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F10/02 C08F2/34 C08F4/642

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 593 083 (UNION CARBIDE CHEMICALS AND PLASTICS COMPANY INC.) 20 April 1994 see tables I,II ---	1-10
X	EP,A,0 582 480 (MITSUI PETROCHEMICAL INDUSTRIES LTD.) 9 February 1994 see example 1 -----	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

6 September 1995

Date of mailing of the international search report

22.09.95

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Serravalle, M

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/07911

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0593083	20-04-94	US-A- 5317036	31-05-94
		AU-B- 657076	23-02-95
		AU-B- 4902893	28-04-94
		BR-A- 9304244	05-07-94
		CA-A- 2108528	17-04-94
		CN-A- 1088939	06-07-94
		CZ-A- 9302179	18-05-94
		FI-A- 934579	17-04-94
		HU-A- 66408	28-11-94
		JP-A- 6192311	12-07-94
		NO-A- 933720	18-04-94
		NZ-A- 248961	26-10-94
EP-A-0582480	09-02-94	JP-A- 6100614	12-04-94
		CA-A- 2101965	07-02-94